

Appendix 4. Quality assurance for volatile organic compound, methane, and inorganic analyses

Quality assurance of water-quality data is an important step in data interpretation. This section describes the quality assurance of the groundwater and surface-water data collected from the West Branch Canal Creek area during 2005. The quality-assured data described in this section include the VOC, methane, and inorganic data. VOC data have undergone independent data-validation procedures and the results are described below.

To determine the reproducibility of analyses, duplicate samples were collected for all methane samples, and VOC samples. Duplicate inorganic samples were collected from approximately 20 percent of the sampled locations. All methane and inorganic duplicates were analyzed, and about 20 percent of VOC duplicates were analyzed. Reproducibility of duplicate samples was determined by measuring the relative percent difference (RPD) between samples by the following calculation:

$$\frac{|C1-C2|}{(C1+C2)/2} \times 100\% = \text{RPD},$$

where C1 is the concentration in the first sample, and C2 is the concentration in the duplicate sample.

Volatile Organic Compound Data

For the period of record, the following blanks were collected: 13 construction blanks for various diffusion samplers, 4 deployment blanks for diffusion samplers, 7 equipment blanks for groundwater sampling, 36 trip blanks for various sampling rounds, and 3 surface-water ISCO VOC trip blanks. Results of these quality-assurance samples showed that seven low-concentration detections of carbon tetrachloride and one low-level concentration of tetrachloroethene in the data set may have been biased high due to detections in an associated blank, and those field values are qualified with a “B” in the data table. Chloroform (CF) was detected in 23 of 64 various blanks at concentrations less than or equal to 1 ug/L but those were confirmed with further analyses to have come from the office deionized water system that was used for all field blanks. These

concentrations did not affect concentrations found in any field or field QA samples. After detecting the CF in the deionized water system, all water used for field and trip blanks were boiled before use and that process eliminated subsequent detection of CF in all the field blanks.

Individual VOC values may be qualified in the data table as being biased high (H) or low (L) based on response to internal calibration standards. Concentrations that may be biased high due to contamination found in associated laboratory blanks are qualified with a “V” in the table.

Duplicate VOC Data Pairs--For routine duplicate samples (not including multiple analyses from the same vials) where samples came from different (subsequent) sample vials, there were 172 data pair sets with 61 parameters giving 10,492 possible comparable data pairs. Of those 10,492 combinations, 973 pairs had detectable concentrations of a given compound for both analyses. Of the 973 pairs, the relative percent differences for 95.5 percent of the samples (910 pairs) were within 25 percent RPD. Sixty three pairs had RPDs greater than (>) 25 percent. Typically, small differences in lower concentrations can result in relatively high RPDs, however, for this data set, of the RPDs greater than 25 percent, a third of the pairs (22) had low concentrations (<10 µg/L), about a third (19) had medium concentrations (between 10 and 100 µg/L), and the other third (22) had higher concentrations (>100 µg/L).

For duplicate pairs where there was a detection in one sample but a ‘<’ value in the associated duplicate (or a detection and a ‘>’ value), most were the result of different dilution factors that were necessary to accurately measure both the low and high concentrations. There were 379 data pairs with a detection in one but a ‘>’ or ‘<’ value in the associated sample. Of those, 320 were in agreement (i.e., a <10.0 µg/L in one sample vs. a concentration of 5.0 µg/L in the duplicate, or a >1,250 µg/L compared to 3,740 µg/L). Thirty-seven pairs agreed within either 10 percent of the detection level or were within 1µg/L of the comparable analysis, and 22 pairs disagreed by more than 10 percent.

Multiple Analyses--When a second analyses is required to be collected from a given vial, these samples are called 'multiple analyses' and are designated as 'MA' in the replicate column in Appendix III. These samples are required when either there was a failure of the initial sample based on internal calibration standards, or when the first sample was run at either too high or too low a dilution to get the best results. These samples are designated as such because of the possibility of losing VOC concentrations from the vial due to either the extraction of the first sample, or because of the resulted head space after the initial sample was collected. The following compares the results when two samples were collected from the same vial.

There were 64 sets of samples where more than one sample was analyzed from the same sample vial. From those 64 sets, there were 303 pairs where there were detections of a compound in both samples. The median RPD for each data pair from the same bottle was calculated, and the average of the 64 median RPDs was 10.3 percent. The RPDs exceeded 25 percent in 48 of the 303 data pairs and of those, two-thirds (32) were from samples with low-concentrations (less than 10 µg/L) where higher RPDs are generally more acceptable. Thirteen pairs with RPDs greater than 25 percent had concentrations between 10 and 100 µg/L, and 3 pairs with RPDs greater than 25 percent had concentrations greater than 100 µg/L.

For pairs where there was a detection in one sample but a 'less-than (<) value in the associated sample (or a detection and a 'greater than' (>) value), most were the result of different dilution factors that were necessary to accurately measure both the low and high concentrations. There were 116 data pairs with a detection in one but a '>' or '<' value in the associated samples. Of those 116 pairs, 110 were in agreement (i.e., a <10.0 µg/L in one sample vs. a concentration of 3.6 µg/L in the duplicate). Four pairs that did not agree but were within 10 percent of each other (detection level vs. detected concentration), or had a difference of less than 1.0 µg/L. Only two duplicate pairs did not agree. One of the two was for the highly volatile compound vinyl chloride. All the vinyl

chloride was lost in that one sample between the times that the first and second were pulled. The other sample that did not agree was for TCE, and the concentration in the second pull from the vial showed an increase in concentration when run at the lower dilution.

Methane Analyses--There were 232 duplicate sample pairs with detectable methane concentrations in both samples. Of those 232 pairs, the RPD of 228 were acceptable (less than 25 percent difference), and 187 of those had RPDs of less than 10 percent. The median of all the RPDs was 4.3 percent. Four pairs exceeded the acceptable range and had RPDs ranging from 32 to 107 percent. The two highest RPDs were from PTN samples.

There were 165 sample pairs where methane concentrations of one or both were below the detection limits. Of those, 156 were in agreement where they were either both below the detection limit, or the one detection was less than the associated 'less than' value (i.e., a <38.1 µg/L in one sample vs. a concentration of 36.6 µg/L in the duplicate). Six pairs agreed either within 10 percent, or within 5µg/L, and two pairs exceeded 10 percent RPD. Of those two, the differences between the "<" value and the detected value were 7 and 12 µg/L.

Inorganic Analyses--Inorganic samples were analyzed by the U.S. Geological National Water Quality Laboratory in Denver, Colorado. For the March and August 2005 groundwater sampling, there were 13 duplicate samples sent to the lab and the analyses are included in Appendix 2. In those 13 samples, there were 207 data pairs with detectable concentrations of a parameter in both samples. Of those 207 pairs, the RPD of 20 samples were greater than 25 percent, and all those were the result of small variability from low concentrations.

Ion balances are used to determine if the cations and anions from the sample balance chemically. These balances are done by comparing milliequivalent concentrations of cations and anions. Given an accurate analysis of a sample and

analyzing enough parameters, the balance should be approximately zero. Balances between -10 and +10 percent are acceptable. Balances greater than 25 percent, or less than -25 percent indicate that either not enough parameters were analyzed, or the analytical results were unacceptable. Negative balances indicate lower concentrations of cations (Ca, Mg, Na, K, Mn, Fe) compared to anions (Cl, SO₄, F, HCO₃). Positive balances indicate lower concentrations of anions compared to cations.

Of the 129 inorganic samples from both groundwater and surface water, all ion balances were within 25 percent, and 74 of those 129 samples were within 10 percent. Of the 81 groundwater samples, ion balances ranged from -16 percent to 5.7 percent, with all but 12 of the balances on the negative side. Of the 48 surface-water samples collected, ion balances, all balances were positive. The noticeable differences between groundwater and surface-water samples indicate that there are analytes that were not analyzed for that likely would have resulted in closer ion balances.

In Appendix II, some values are missing and described as either 'O-deleted' or 'U-deleted'. The O-deleted qualifiers indicate that not enough water was available to complete the analyses. The U-deleted qualifier indicates that the lab was unable to determine the concentrations due to interference from other compounds.